Organic-Inorganic Hybrid Solar Cells: State of the Art, Challenges and Perspectives

Yunfei Zhou, Michael Eck and Michael Krüger
University of Freiburg/Freiburg Materials Research Centre
Germany

1. Introduction

Novel photovoltaic (PV) technologies are currently investigated and evaluated as approaches to contribute to a more environmental friendly energy supply in many countries. One of the driving forces are the aims to reduce the emission of green house gases and the dependency on importing fossil energy resources from political unstable countries. Additionally the wish to replace nuclear power by greener and less threatening technologies will enhance the development of regenerative energy supply in many countries especially after the recent nuclear catastrophe at Fukushima nuclear power plant in Japan in March 2011. This will include the more rapid implementation of existing mature PV technologies but also the development and improvement of novel PV approaches such as organic PV (OPV) and dye-sensitized solar cells (DSSCs) together with new efficient strategies for energy storage and distribution to make electric power, deriving from PVs, available whenever and wherever it is needed.

The so-called 1st generation of solar cells based on e.g. bulk crystalline and polycrystalline silicon is still dominating the PV market. However, so-called 2nd generation solar cells mainly consisting out of thin film solar cells based on CdTe, Copper Indium Gallium Selenide (CIGS), and amorphous silicon gained distribution of ca. 25% in market share today worldwide. It is expected that this number will increase significantly within the next years. While for the 1st and 2nd generation solar cells commercial solar panels are available with decent power conversion efficiencies (PCEs) and lifetimes, the emerging 3rd generation solar cells such as OPV and DSSCs technologies are still in the development phase. Some commercially available products have recently entered the market such as e.g. solar bags representing niche products, which are so far not suitable for competing with traditional large scale applications of solar panels of the 1st and 2nd generations. In traditional solar panels the differences between best solar cell and average solar cell efficiencies are much smaller than for the emerging solar cell technologies with the consequence that modules of 3rd generation solar cells still suffer from too low performance. In Table 1 the best cell and module efficiencies of different PV technologies are compared. It has to be mentioned that especially for the emerging new PV technologies the average efficiencies are significantly lower than the results of the best cells.
2. Device structures and working principle

Organic-inorganic hybrid solar cells are typically thin film devices consisting out of photoactive layer(s) between two electrodes of different work functions. High work function, conductive and transparent indium tin oxide (ITO) on a flexible plastic or glass substrate is often used as anode. The photoactive light absorbing thin film consists out of a conjugated polymer as organic part and an inorganic part out of e.g. semiconducting nanocrystals (NCs). A top metal electrode (e.g. Al, LiF/Al, Ca/Al) is vacuum deposited onto the photoactive layer finally. A schematic illustration of a typical device structure is shown in Fig. 1a. Generally there are two different structure types for photoactive layers - the bilayer structure (Fig. 1b) and the bulk heterojunction structure (Fig. 1c). The latter one is usually realized by just blending the donor and acceptor materials and depositing the blend on a substrate. In contrast to bulk inorganic semiconductors, photon absorption in organic semiconductor materials does not generate directly free charge carriers, but strongly bound electron-hole pairs so-called excitons (Gledhill et al., 2005). Since the exciton diffusion lengths in conjugated polymers are typically around 10-20 nm (Halls et al., 1996) the optimum distance of the exciton to the donor/acceptor (D/A) interface, where charge transfer can take place and excitons dissociate into free charge carriers, should be in the same length range. Therefore the bulk-heterojunction structure was introduced where the electron donor and acceptor materials are blended intimately together (Halls et al., 1995). The interfacial area is dramatically increased and the distance that excitons have to travel to reach the interface is reduced. After exciton dissociation into free charge carriers, holes and electrons are transported via polymer and NC percolation pathways towards the respective electrodes. Ideally, an interdigital donor acceptor configuration would be a perfect structure for efficient exciton dissociation and charge transport (Fig. 1d). In such a structure, the distance from exciton generation sites, either in the donor or the acceptor phase, to the D/A
interface would be in the range of the exciton diffusion length. After exciton dissociation, both holes and electrons will be transported within their pre-structured donor or acceptor phases along a direct percolation pathway to the respective electrodes. This interdigital structure can be realized by various nanostructuring approaches, which will be discussed in detail later in the section 6.2.2.

![Schematic illustration of typical device structures for hybrid solar cells.](image)

In hybrid solar cells, photocurrent generation is a multistep process. Briefly, when a photon is absorbed by the absorbing material, electrons are exited from the valence band (VB) to the conduction band (CB) to form excitons. The excitons diffuse to the donor/acceptor interface where charge transfer can occur leading to the dissociation of the excitons into free electrons and holes. Driven by the internal electric field, these carriers are transported through the respective donor or acceptor material domains and are finally collected at the respective electrodes. To sum up, there are four main steps: photon absorption, exciton diffusion, charge separation as well as charge carrier transport and collection. The physics of organic/hybrid solar cells is reviewed in detail elsewhere (Greenham, 2008; Saunders & Turner, 2008).

3. Donor-acceptor materials

Due to the decreased size of NCs down to the nanometer scale, quantum effects occur, thus a number of physical (e.g. mechanical, electrical, optical, etc.) properties change when compared to those of bulk materials. For example, the quantum confinement effect (Brus, 1984) can be observed once the diameter of the material is in the same magnitude as the wavelength of the electron wave function. Along with the decreasing size of NCs, the energy levels of NCs turn from continuous states to discrete ones, resulting in a widening of the band gap apparent as a blue shift in the absorption and photoluminescence (PL) spectra. In general, there are two distinct routes to produce NCs: by physical approaches where they can be fabricated by lithographic methods, ion implantation, and molecular beam deposition; or by chemical approaches where they are synthesized by colloidal chemistry in
solution. Colloidal synthetic methods are widely used and are promising for large batch production and commercial applications. The unique optical and electrical properties of colloidal semiconductor NCs have attracted numerous interests and have been explored in various applications like light-emitting diodes (LEDs) (Kietzke, 2007), fluorescent biological labeling (Bruchez et al., 1998), lasers (Kazes et al., 2002), and solar cells (Huynh et al., 2002). Colloidal NCs synthesized in organic media are usually soluble in common organic solvents thus they can be mixed together with conjugated polymers which are soluble in the same solvents. With suitable band gap and energy levels, NCs can be incorporated into conjugated polymer blends to form so-called bulk-heterojunction hybrid solar cells (Borchert, 2010; Reiss et al., 2011; Xu & Qiao, 2011; Zhou, Eck et al., 2010). CdS, CdSe, CdTe, ZnO, SnO$_2$, TiO$_2$, Si, PbS, and PbSe NCs have been used so far as electron acceptors. In Table 2 different donor-acceptor combinations in 3rd generation solar cells are shown together with the respective highest achieved PCEs from laboratory devices.

Bulk-heterojunction hybrid solar cells are still lagging behind the fullerene derivative-based OPVs in respect of device performance. Nevertheless, they have the potential to achieve better performance while still maintaining the benefits such as potentially low-cost, thin and flexible, and easy to produce. By tuning the diameter of the NCs, their band gap as well as their energy levels can be varied due to the quantum size effect. Furthermore, quantum confinement leads to an enhancement of the absorption coefficient compared to that of the bulk materials (Alivisatos, 1996). As a result, in the NCs/polymer system, both components have the ability to absorb incident light, unlike the typical polymer/fullerene system where the fullerene contributes very little to the photocurrent generation (Diener & Alford, 1998; Kazaoui & Minami, 1997). In addition, NCs can provide stable elongated structures on the length scale of 2-100 nm with desirable exciton dissociation and charge transport properties (Huynh et al., 2002).

<table>
<thead>
<tr>
<th>Donor</th>
<th>Acceptor</th>
<th>PCE(%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>C$_{60}$ derivative</td>
<td>8.3</td>
<td>(Konarka, 2010)</td>
</tr>
<tr>
<td>Polymer</td>
<td>CdSe Tetrapods</td>
<td>3.19</td>
<td>(Dayal et al., 2010)</td>
</tr>
<tr>
<td>Polymer</td>
<td>Polymer</td>
<td>2.0</td>
<td>(Frechet et al., 2009)</td>
</tr>
<tr>
<td>Small molecule</td>
<td>Small molecule</td>
<td>8.3</td>
<td>(Heliatek, 2010)</td>
</tr>
<tr>
<td>Dye</td>
<td>TiO$_2$</td>
<td>11.2</td>
<td>(Han et al., 2006)</td>
</tr>
</tbody>
</table>

Table 2. Donor-acceptor combinations and best PCEs of 3rd generation solar cells.

Fig. 2 illustrates commonly used donor and acceptor materials in bulk-heterojunction hybrid solar cells. The conjugated polymers usually act as electron donors and semiconductor NCs with different shapes such as spherical quantum dots (QDs), nanorods (NRs) and tetrapods (TPs) as well as the C$_{60}$ derivative PCBM as electron acceptor materials.

In Fig. 3 the energy levels (in eV) of commonly used conjugated polymers as donors and NCs as acceptors for bulk-heterojunction hybrid solar cells are summarized and compared. The Fermi levels of the electrodes and the energy levels of PCBM are shown as well. The variation of the values for the energy levels are deriving from different references and are due to different applied measurement methods for extracting the respective values of the lowest unoccupied molecular orbitals and highest occupied molecular orbitals (HOMO-LUMO) levels such as cyclic voltammetry (CV), X-ray photoelectron spectroscopy (XPS), ultra-violet photoelectron spectroscopy (UPS). The data for the respective HOMO-LUMO levels have been extracted from various references which are given in a recent review article (Zhou, Eck et al., 2010).
Fig. 2. Up: Chemical structures of commonly used conjugated polymers as electron donors for bulk-heterojunction hybrid solar cells. Shown are Poly(3-hexylthiophene-2,5-diyl) (P3HT), Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene](MEH-PPV), and Poly[2,6-(4,4-bis-(2-ethylhexy)-4H-cyclopenta[2,1-b;3,4-b]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)](PCPDTBT). Down: Differently shaped semiconductor NCs as well as the chemical structure of [6,6]-Phenyl C₆₁ butyric acid methyl ester (PCBM) as electron acceptors.

Fig. 3. Energy levels (in eV) of commonly used conjugated polymers as electron donors and NCs as electron acceptors in bulk-heterojunction hybrid solar cells.
Energy levels of donor and acceptor materials should match for efficient charge separation at the D/A interface. PL spectroscopy is a simple and useful method to investigate if a material combination can be an appropriate D/A system (Greenham et al., 1996). Because pure polymers such as P3HT and MEH-PPV exhibit a strong PL behaviour, its PL intensity is quenched by the addition of NCs with matching energy levels. This is an indication that charge transfer occurs from polymer to NCs. However, the observation of PL quenching is not necessarily a proof of charge separation within the D/A system because Förster resonance energy transfer (FRET) could also happen from larger band gap materials to smaller band gap materials, leading to strong PL quenching as well (Greenham et al., 1996). Therefore, additional methods such as photoinduced absorption (PIA) spectroscopy and light-induced electron spin resonance (L-ESR) spectroscopy are used in order to exclude PL quenching due to FRET. A detailed review on these two methods has been recently published (Borchert, 2010).

4. CdSe NCs based hybrid solar cells

CdSe NCs were the first NCs being incorporated into solar cells which still exhibit the highest PCEs compared to devices with NCs from other materials, and are still under extensive studies for utilization in hybrid solar cells. CdSe NCs have some advantages: they absorb at a useful spectral range for harvesting solar emission from 300 nm to 650 nm, they are good electron acceptors in combination with conjugated polymers, and the synthetic methods for their synthesis are well-established. The incorporation of CdSe spherical quantum dots into polymer for hybrid solar cells was firstly reported in 1996 (Greenham et al., 1996). At a high concentration of NCs of around 90% by weight (wt%), external quantum efficiencies (EQE) up to 10% were achieved, indicating an efficient exciton dissociation at the polymer/NCs interface. Although the phase separation, between the polymer and the NCs was observed to be in the range of 10-200 nm, the PCEs of devices were very low of about 0.1%. This was attributed to an inefficient electron transport between the individual NCs. After different shapes of NCs were synthetically available (Peng X. G. et al., 2000), different elongated CdSe structures were utilized in hybrid solar cells as electron acceptor materials. Meanwhile numerous approaches were published regarding the synthesis of various morphologies and structures of CdSe NCs such as QDs, NRs and TPs and their application in hybrid solar cells. A significant advance was reported in 2002 (Huynh et al., 2002), when efficient hybrid solar cells based on elongated CdSe NRs and P3HT were obtained. Elongated NRs were used for providing elongated pathways for effective electron transport. Additionally, P3HT was used as donor material instead of MEH-PPV since it has a comparatively high hole mobility and absorbs at a longer wavelength range compared to PPV derivatives (Schilinsky et al., 2002). By increasing the NRs length, improved electron transport properties were demonstrated resulting in an improvement of the EQE. The optimized devices consisting out of 90wt% pyridine treated nanorods (7 nm in diameter and 60 nm in length) and P3HT exhibited an EQE over 54% and a PCE of 1.7%. Later on, 1,2,4-trichlorobenzene (TCB), which has a high boiling point, was used as solvent for P3HT instead of chlorobenzene. It was found that P3HT forms fibrilar morphology when TCB was used as solvent providing extended pathways for hole transport, which resulted in improved device efficiencies up to 2.6% (Sun & Greenham, 2006). Further improvement was achieved by using CdSe TPs, since TPs always have an extension perpendicular to the electrode for more efficient electron transport in comparison to NRs which are preferentially

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oriented more parallel to the electrode (Hinds et al., 2011). Devices based on pyridine treated CdSe TPs exhibited efficiencies up to 2.8% (Sun et al., 2005). Recently, by using the lower band gap polymer PCPDTBT, which can absorb a higher fraction of the solar emission, an efficiency of 3.19% was reported (Dayal et al., 2010). This value is up to date the highest efficiency for colloidal NCs based bulk-heterojunction hybrid solar cells. Elongated or branched NCs in principal can provide more extended and directed electrical conductive pathways, thus reducing the number of inter-particle hopping events for extracting electrons towards the electrode. However, device performance does not only benefit from the shape of the NCs, but also from their solubility and surface modification which influence significantly the charge transfer and carrier transport behavior. Despite the relatively high intrinsic conductivity within the individual NCs, the electron mobility through the NC network in hybrid solar cells is quite low, which could be mainly attributed to the electrical insulating organic ligands on the NC surface. Ginger et al. have investigated charge injection and charge transfer in thin films of spherical CdSe NCs covered with TOPO ligand sandwiched between two metal electrodes (Ginger & Greenham, 2000). Very low electron mobilities in the order of $10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ were measured, whereas the electron mobility of bulk CdSe is in the order of $10^2$ cm$^2$V$^{-1}$s$^{-1}$ (Rode, 1970). In most cases, the ligands used for preventing aggregation during the growth of the NCs contain long alkyl chains, such as oleic acid (OA), trioctylphosphine oxide (TOPO) or hexadecylamine (HDA), form electrically insulating layers preventing an efficient charge transfer between NCs and polymer, as well as electron transport between the individual NCs (Greenham et al., 1996; Huynh et al., 2003). In order to overcome this problem, post-synthetic treatment on the NCs has been investigated extensively. Fig. 4 shows two general strategies of post-synthetic treatment on NCs for improving the performance of hybrid solar cells – ligand exchange from original long alkyl ligands to shorter molecules e.g. pyridine, and chemical surface treatment and washing for reducing the ligand shell. A combination of ligand shell reduction and ligand exchange afterwards might further improve the solar cell performance by enhancing the electron transport in the interconnected NC network.

Fig. 4. Schematic illustration of two post-synthetic QD treatment strategies to enhance the PCEs in hybrid solar cells: ligand exchange (up) and reduction of the ligand surface of QDs by applying a washing procedure (middle). A combination of the two approaches might be beneficial for further enhancing the performance of hybrid solar cells (down).
Pyridine ligand exchange is the most commonly used and effective postsynthetic procedure so far, leading to the state-of-the-art efficiencies for hybrid solar cells (Huynh et al., 2002). Generally, as-synthesized NCs are washed by methanol several times and consequently refluxed in pure pyridine at the boiling point of pyridine under inert atmosphere overnight. This pyridine treatment is believed to replace the synthetic insulating ligand with shorter and more conductive pyridine molecules.

Treatments with other materials such as chloride (Owen et al., 2008), amine (Olson et al., 2009), and thiols (Aldakov et al., 2006; Sih & Wolf, 2007) were also investigated. Aldakov et al. systematically investigated CdSe NCs modified by various small ligand molecules with nuclear magnetic resonance (NMR), optical spectroscopy and electrochemistry, although their hybrid devices exhibited low efficiencies (Aldakov et al., 2006). Olson et al. reported on CdSe/P3HT blended devices exhibiting PCEs up to 1.77% when butylamine was used as a shorter capping ligand for the NCs (Olson et al., 2009). In an alternative approach, shortening of the insulating ligands by thermal decomposition was demonstrated and led to a relative improvement of the PCEs of the CdSe/P3HT-based solar cells (Seo et al., 2009).

However, NCs after ligand exchange with small molecules tend to aggregate and precipitate out of the organic solvent because long alky chain ligands are replaced (Huynh et al., 2002; Huynh et al., 2003), resulting in difficulties to obtain stable mixtures of NCs and polymer. Recently, a new strategy for post-synthetic treatment on spherical CdSe QDs was demonstrated (Zhou, Riehle et al., 2010), where the NCs were treated by a simple and fast hexanoic acid-assisted washing procedure. One advantage of avoiding the exchange of the synthesis capping ligands is that the QDs retain a good solubility after acid treatment, resulting in reproducible performance as well as allowing a high loading of the CdSe QDs in the blend, which is preferable for an efficient percolation network formation during the annealing step of the photoactive composite film. Devices with optimized ratios of QDs to P3HT exhibited reproducible PCEs up to 2.1% after spectral mismatch correction (Zhou, Riehle et al., 2010) (Fig. 5a). This is the highest reported value for a CdSe QD / P3HT based hybrid solar cell so far. It is notable that the FF is relatively high up to 0.54, implying a good charge carrier transport capability in the devices. A simple reduced ligand sphere model was proposed to explain the possible reason for improved photovoltaic device efficiencies after acid treatment as shown in Fig. 5b (Zhou, Riehle et al., 2010). By the assistance of hexanoic acid this “immobilized” insulating spheres formed by HDA ligands are effectively reduced in size due to the salt formation of HDA. This organic salt is also much more easily dissolved in the supernatant solution than unprotonated HDA and can be separated easily from the QDs by subsequent centrifugation.

In addition, extended investigations on TOP/OA capped CdSe QDs suggested that the hexanoic acid treatment is also for this ligand system applicable for improving the device performance. Although these two kinds of QDs have different sizes (5.5 nm for HDA-capped QDs and 4.7 nm for TOP/OA capped QDs) which could result in different energy levels of QDs as well, after acid treatment both devices exhibit PCEs of 2.1% (Zhou et al., 2011) as shown in Fig. 6. Furthermore, using low band gap polymer PCPDTBT, optimized devices based on acid treated TOP/OA CdSe QDs were achieved and exhibited the highest efficiency of 2.7% for CdSe QD based devices so far (Zhou et al., 2011).
5. Hybrid solar cells based on other NCs

Other semiconductor NCs than CdSe were also used for hybrid solar cells. ZnO NCs have attracted a lot of attention because they are less toxic than other II-VI semiconductors and are relatively easy to synthesize in large quantities. Devices based on blends of MDMO-PPV and ZnO NCs at an optimized NC content (67 wt%) presented a PCE of 1.4% (Beek et al., 2004). By using P3HT as donor polymer which has a higher hole mobility together with an in-situ synthesis approach of ZnO directly in the polymer matrix, the efficiency was optimized up to 2% using a composite film containing 50 wt% ZnO NCs (Oosterhout et al., 2009). However, because of the relatively large band gap, the contribution to the absorption of light from ZnO NCs is very low. Another disadvantage is the low solubility of ZnO NCs in solvents which are commonly used for dissolving conjugated polymers (Beek et al., 2006).
This problem of processing ZnO NCs together with polymers to obtain well-defined morphologies limits up to now the further improvement of the solar cell performance of ZnO based hybrid solar cells.

Low band gap NCs such as CdTe, PbS, PbSe, CuInS$_2$ and CuInSe$_2$ NCs are promising acceptor materials due to their ability of absorbing light at longer wavelengths which may allow an additional fraction of the incident solar spectrum to be absorbed. For instance, CdTe NCs have a smaller band gap compared to CdSe NCs, while their synthesis routes are similar to CdSe NCs (Peng & Peng, 2001). However, suitable CdTe/polymer systems have not yet been found, and reported PCEs based on CdTe/MEH-PPV are quite below 0.1% (Kumar & Nann, 2004). A systematic investigation on hybrid solar cells based on MEH-PPV blended with CdSe$_{1-x}$Te$_{x}$ tetropods demonstrated a steady PCE decrease from 1.1% starting from CdSe to 0.003% with CdTe (Zhou et al., 2006). The reason of the dramatically decrease in efficiency could be attributed to the possibility that energy transfer rather than charge transfer could occur from the polymer to CdTe NCs in CdTe/Polymer blends, resulting in an insufficient generation of free charge carriers (van Beek et al., 2006; Zhou et al., 2006). However there is one work reporting over 1% efficiency using vertically aligned CdTe nanorods combined with poly(3-octylthiophene) (P3OT), indicating that CdTe NCs may be useful for hybrid solar cells when the energy levels are matching to the polymers (Kang et al., 2005). Further lowering of the NC band gap could be achieved by using semiconductors such as PbS or PbSe. Watt et al. have developed a novel surfactant-free synthetic route where PbS NCs were synthesized in situ within a MEH-PPV film (Watt et al., 2004; Watt et al., 2005). CuIn$_2$S$_2$ and CuInSe$_2$ which have been successfully used in inorganic thin film solar cells are promising for hybrid solar cells as well. Although an early study performed by Arici et al. (Arici et al., 2003) showed very low efficiencies <0.1%, recent progress on colloidal synthesis methods for high quality CuInS$_2$ (Panthani et al., 2008; Yue et al., 2010) might stimulate the development to more efficient photovoltaic devices. In general, using low band gap NCs as electron acceptors in polymer/NCs systems has been not successful yet, because energy transfer from polymer to low band gap NCs is the most likely outcome, resulting in inefficient exciton dissociation.

Recently it has been demonstrated that Si NCs are a promising acceptor material for hybrid solar cells due to the abundance of Si compounds, non-toxicity, and strong UV absorption. Hybrid solar cells based on blends of Si NCs and P3HT with a PCE above 1% have been reported (Liu et al., 2009). Si NCs were synthesized by radio frequency plasma via dissociation of silane, and the size can be tuned between 2 nm and 20 nm by changing chamber pressure, precursor flow rate, and radio frequency power. Devices made out of 50 wt% Si NCs, 3-5 nm in size, exhibited a PCE of 1.47% under AM1.5 G illumination which is a promising result (Liu et al., 2010).

The distribution of ligand-free NCs into the conjugated polymer matrix should be of great advantage for the resulting hybrid solar cells. This can be realized by an “in situ” synthesis approach of NCs directly in the polymer matrix. First attempts have been performed with a one pot synthesis of PbS in MEH-PPV by Watt et al. (Watt et al. 2005). Although the size distribution and concentration of synthesized NCs was not optimized, a PCE of 1.1 % was reached using this method. Liao et al. demonstrated successfully a direct synthesis of CdS nanorods in P3HT, leading to hybrid solar cells with PCEs up to 2.9% (Liao et al., 2009).

Table 3 summarized the selected performance parameters of hybrid solar cells based on colloidal NCs and conjugated polymers.
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Table 3. Selected performance parameters of hybrid solar cells reported in literature based on colloidal NCs and conjugated polymers.

<table>
<thead>
<tr>
<th>NC</th>
<th>Shape</th>
<th>Polymer</th>
<th>PCE(%)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>CdSe</td>
<td>TP</td>
<td>PCPDTBT</td>
<td>3.19</td>
<td>(Dayal et al., 2010)</td>
</tr>
<tr>
<td>CdSe</td>
<td>TP</td>
<td>OG$<em>{1}$C$</em>{10}$PPV</td>
<td>2.8</td>
<td>(Sun et al., 2005)</td>
</tr>
<tr>
<td>CdSe</td>
<td>QD</td>
<td>PCPDTBT</td>
<td>2.7</td>
<td>(Zhou et al., 2011)</td>
</tr>
<tr>
<td>CdSe</td>
<td>NR</td>
<td>P3HT</td>
<td>2.65</td>
<td>(Wu &amp; Zhang, 2010)</td>
</tr>
<tr>
<td>CdSe</td>
<td>NR</td>
<td>P3HT</td>
<td>2.6</td>
<td>(Sun &amp; Greenham, 2006)</td>
</tr>
<tr>
<td>CdSe</td>
<td>TP</td>
<td>APFO-3</td>
<td>2.4</td>
<td>(Wang et al., 2006)</td>
</tr>
<tr>
<td>CdSe</td>
<td>Hyperbranched</td>
<td>P3HT</td>
<td>2.2</td>
<td>(Gur et al., 2007)</td>
</tr>
<tr>
<td>CdSe</td>
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<td>(Zhou, Riehle et al., 2010)</td>
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<tr>
<td>CdSe</td>
<td>QD</td>
<td>P3HT</td>
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<td>(Olson et al., 2009)</td>
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<tr>
<td>CdSe</td>
<td>NR</td>
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<td>(Huynh et al., 2002)</td>
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<tr>
<td>ZnO</td>
<td>-</td>
<td>P3HT</td>
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<td>(Oosterhout et al., 2009)</td>
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<tr>
<td>ZnO</td>
<td>-</td>
<td>P3HT</td>
<td>1.4</td>
<td>(Beek et al., 2004)</td>
</tr>
<tr>
<td>CdS</td>
<td>NR</td>
<td>P3HT</td>
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<td>(Liao et al., 2009)</td>
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<tr>
<td>CdTe</td>
<td>NR</td>
<td>MEH-PPV</td>
<td>0.05</td>
<td>(Kumar &amp; Nann, 2004)</td>
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<tr>
<td>CdTe</td>
<td>NR</td>
<td>P3OT</td>
<td>1.06</td>
<td>(Kang et al., 2005)</td>
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<tr>
<td>PbS</td>
<td>QD</td>
<td>MEH-PPV</td>
<td>0.7</td>
<td>(Gunes et al., 2007)</td>
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<tr>
<td>PbSe</td>
<td>QD</td>
<td>P3HT</td>
<td>0.14</td>
<td>(Cui et al., 2006)</td>
</tr>
<tr>
<td>Si</td>
<td>QD</td>
<td>P3HT</td>
<td>1.47</td>
<td>(Liu et al., 2010)</td>
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</table>

6. Challenges and perspectives

6.1 Extension of the photon absorption and band gap engineering

Absorption of a large fraction of the incident photons is required for harvesting the maximum possible amount of the solar energy. Generally, incident photons are mainly absorbed by the donor polymer materials and partially also from the inorganic NCs. For example in blends containing 90 wt% CdSe nanoparticles in P3HT, about 60% of the total absorbed light energy can be attributed to P3HT due to its strong absorption coefficient (Dayal et al., 2010). Using P3HT as donor polymer, hybrid solar cells with spherical QDs, NRs, and hyperbranched CdSe NCs exhibited the best efficiencies of 2.0% (Zhou, Riehle et al., 2010), 2.6% (Sun & Greenham, 2006; Wu & Zhang, 2010), and 2.2% (Gur et al., 2007), respectively. However, due to the insufficient overlap between the P3HT absorption spectrum and the solar emission spectrum (Scharber et al., 2006), further improving of the PCE values seems to be difficult to obtain with this polymer system.

Assuming that all photons up to the band gap edge are absorbed and converted into electrons without any losses (i.e. external quantum efficiency (EQE) is constant 1), crystalline silicon with a band gap of 1.1 eV can absorb up to 64% of the photons under AM1.5 G illumination, with a theoretical achievable current density $J_{sc}$ of about 45 mA/cm$^2$. While in the case of P3HT having a band gap of 1.85 eV, only 27% photons can be absorbed, resulting in a maximal $J_{sc}$ of 19 mA/cm$^2$. By using a low band gap polymer with a band gap of e.g. about 1.4 eV, 48% photons can be absorbed leading to a maximum $J_{sc}$ up to 32 mA/cm$^2$ (Zhou, Eck et al., 2010). Nevertheless, lowering the band gap of photo-absorbing materials below a certain limit will lead to a decrease in device efficiency, because the energy of absorbed photons with a larger energy than the band gap will be wasted as the electrons and holes relax to the band edges.
Most low band gap polymers are from the material classes of thiophene, fluorene, carbazole, and cylopentadithiophene based polymers, which are reviewed in detail in several articles (Kamat, 2008; Riede et al., 2008; Scharber et al., 2006). Among those low band gap polymers, PCPDTBT (chemical structure shown in Fig.2) with a band gap of ~1.4 eV and a relatively high hole mobility up to 1.5×10^{-2} cm^{2}V^{-1}s^{-1} (Morana et al., 2008) appears to be an excellent candidate as a photon-absorbing and electron donating material (Soci et al., 2007). OPVs based on PCPDTBT:PC_{70}BM system achieved already efficiencies up to 5.5% (Peet et al., 2007) and 6.1% (Park et al., 2009). Recently, a bulk-heterojunction hybrid solar cell based on CdSe tetrapods and PCPDTBT was reported by Dayal et al. (Dayal et al., 2010) with an efficiency of 3.13%. Devices based on PCPDTBT and CdSe TPs, exhibited an EQE of >30% in a broad range from 350 nm to 800 nm, which is the absorption band of the polymer. It is notable that the devices reached very high J_{sc} values above 10 mA/cm^{2}, indicating that the broad absorption ability of the photoactive hybrid film consequently contributes to the photocurrent. Zhou et al. reported on a direct comparison study of using PCPDTBT and P3HT as donor polymer for CdSe QDs based hybrid solar cells (Zhou et al., 2011). Fig. 7a shows the comparison of the best cells fabricated from blends of P3HT:CdSe and PCPDTBT:CdSe. The PCPDTBT based device showed a considerable enhancement of PCE to 2.7% compared to the P3HT based device mainly due to the increase of J_{sc}. Fig. 7b shows the EQE spectrum of photovoltaic devices comparing the two different polymers. The PCPDTBT based device showed a broader EQE spectrum from 300 nm to 850 nm, and considerable photocurrent contribution from the QDs was observed at 400 nm region where the QD absorption is strong. This implies that both components of the PCPDTBT:CdSe system contribute to the absorption of incident photons and to the photocurrent generation. The energy levels of donor and acceptor materials also play an important role determining the V_{oc} and consequently device efficiency. The optimum LUMO offset between donor and acceptor has been investigated by many research groups. An offset energy of 0.3 eV was found to be sufficient for charge transfer (Brabec et al., 2002; Bredas et al., 2004). Therefore, fitting of the donor and acceptor energy levels as well as band gap engineering are desirable for eliminating energy losses during the charge transfer process. Scharber et al. demonstrated a relationship between PCEs of solar cells, band gaps, and the offsets between donor and acceptor LUMO levels of the donor materials.

As a result, for PCEs of devices exceeding 10%, a donor band gap <1.74 eV and a LUMO level <-3.92 eV are required (Scharber et al., 2006). In addition, Dennler et al. demonstrated
that for a minimum energy offset of 0.3 eV between the donor and acceptor LUMO levels, PCEs of >10% are practical available for a donor polymer with an ideal optical band gap of ~1.4 eV (Riede et al., 2008). Recently, Xu et al. predicted the highest achievable cell efficiencies in polymer/NCs hybrid solar cells by considering the polymer band gaps and polymer LUMO energy levels (Xu & Qiao, 2011). Fig. 9 illustrates the 3D contour plots of polymer LUMO levels, polymer band gaps, and calculated device efficiencies for three representative inorganic NCs with CBs at ~4.2 eV (TiO$_2$), ~4.4 eV (ZnO) and ~3.7 eV (CdSe). Assuming all of the photons are absorbed by the polymers and the $V_{oc}$ equals to the energy offset between the polymer HOMO and the NC LUMO, device efficiencies beyond 10% can be achieved by using polymers with optimal band gaps and LUMO levels.

Another approach to increase the photon absorption in the active layer is to use light trapping structures as substrates or as electrodes. Light trapping can be used to overcome the problem of insufficient absorption in thin film solar cells in general (Rim et al., 2007). Nano- and microstructures of the photoactive film material can be utilized to enlarge the total pathway of incident light through the active layer. An early attempt for realizing a light trapping structure in organic solar cells was made by Roman et al. (Roman et al., 2000), who used a sub micrometer patterned grating created by lithography to mold the active layer in a way that it exhibits a cross sectional saw tooth characteristic on its surface. The subsequently deposited aluminum top electrode is then acting as a reflective layer. Furthermore Niggemann et al. created buried nanoelectrodes (Niggemann et al., 2004) requiring an inverted cell design by using a structured aluminium coated electrode, and microprisms (Niggemann et al., 2008) as light trapping substrate for organic solar cells. So far light trapping was only applied on pure organic solar cells, but because of the similar device structure these attempts can also be applied to hybrid solar cells.

6.2 Enhancing of the charge carrier transport in hybrid solar cells
The film morphology plays a decisive role in the performance of a hybrid solar cell. Both the nano-phase separation and the charge extraction must be optimized for a highly efficient solar cell. For an optimal nano-phase separation the acceptor material must be homogeneously distributed in the blend. For optimizing the charge extraction towards the electrodes, continuous percolation pathways should exist for the charges to move towards...
the respective electrodes. For optimized hybrid films with suitable nano-phase separation the solvents used for the donor-acceptor blends must suit well for both the NCs and the polymer. In order to improve the dispersibility of the NCs inside the NC/polymer mixture, pyridine is added in a certain optimal concentration to the P3HT solvent chloroform. The experiment resulted in a reduction of the surface roughness of the hybrid film which was measured by AFM and in a higher EQE for hybrid devices (Huynh et al., 2003). The crystallinity of the conjugated polymer is another important factor to consider for improving the hole extraction towards the anode of the solar cell. Therefore P3HT is a suitable material (Sharma et al., 2010). Greenham’s group reported that using TCB as a solvent with a slow evaporation rate, in contrast to chloroform, is enhancing the self organization of the polymer and thereby the efficiency of a P3HT/CdSe (NR) solar cell (Sun & Greenham, 2006). Additionally during the thermal treatment interfacial and access ligands (e.g. pyridine) are removed (Huynh et al., 2003). By treating the blend at temperatures of ca. 110°C it is reported that oxygen is removed from the P3HT (Olson et al., 2009). Erb et. al reported that the crystallinity of P3HT is improving significantly after thermal annealing which can be observed by the extension of the absorption spectra to longer wavelengths after thermal treatment of the polymer (Erb et al., 2005).

6.2.1 Visualization of the nanomorphology of thin hybrid films

An AFM analysis of the active layer of the hybrid blend reveals information about the surface topography. Here the roughness is mostly regarded as indicator for the quality of the nanophase separation of NC and polymer phases. An AFM image of the surface of a CdSe/P3HT hybrid film is shown in Fig. 9a. In addition TEM can be used for the investigation of thin hybrid films. The two dimensional image delivers information about the distribution of donor and acceptor materials in the film (Fig. 9b). Hereby the quality of the mixing and the tendency of NC aggregation as well as nanophase separation can be observed. A relatively new approach for the analysis of the nanomorphology in hybrid solar cells is the use of 3D TEM tomography, where a series of TEM images are taken of the sample subsequently at different tilt angles.

![AFM image](image1.png)

![TEM image](image2.png)

Fig. 9. (a) AFM image of the surface of a spin coated CdSe/P3HT blend film, (b) TEM of a CdSe/P3HT thin film. The white areas represent the polymer phase and the dark areas the NC phase.

With the help of a computer software a three dimensional tomographic view of the donor-acceptor blend can be achieved (Fig. 10). This method is especially well suited for hybrid solar cells because they exhibit a high contrast between the inorganic NCs and the organic...
polymer. The obtained visualization of the internal material distribution gives an important feedback for solar cell development. In Fig. 10a a 3D visualization of a P3HT/ZnO thin hybrid film is shown (Oosterhout et al., 2009). The volume fraction of NCs present in the active area could be successfully extracted. Furthermore the fraction of NCs connected to the top electrode could be calculated, which was decreasing from 93% for a 57 nm thin film to 80% for a 167 nm thin film. This decrease could be correlated with the decrease of the IQE. Surprisingly despite of the better IQE, thinner films are showing a considerably coarser nanophase separation with only 60% of the fraction of the P3HT lying at a distance of 10 nm or less to the next acceptor, while this value was nearly 100% for the 167 nm thick film.

Fig. 10b shows analyzed blends of O=C$_1$C$_{10}$-PPV/CdSe by 3D TEM tomography (Hindson et al., 2011). It was demonstrated that the better performance of CdSe NR based devices is due to the higher connectivity between the NCs leading to a total fraction of ca. 90% NRs being connected to the top electrode while for QD based cells the fraction of connected NCs for the same weight ratio was found to be only 78%. It was additionally found that the alignment of the NRs is mostly horizontal, since 82% are aligned within 10° of the x-y-plane.

Fig. 10. (a) 3D visualizations of the a hybrid P3HT/ZnO hybrid film. Reprinted by permission from Macmillan Publishers Ltd: [Nature Materials] (Oosterhout et al., 2009), copyright (2009); (b) Distribution of NRs within a O=C$_1$C$_{10}$-PPV/CdSe-NR hybrid film based on TEM tomography. Reprinted with permission from (Hindson et al., 2011). Copyright 2011 American Chemical Society.

6.2.2 Morphology control by nanostructuring approaches

Morphology control on the nanoscale is a key issue to reduce the recombination of excitons. The optical absorption length within the donor material of the film is of about 100 nm (Peumans et al., 2003), while the generated excitons have a diffusion length of only 10 nm to 20 nm (Halls et al., 1996). Even if an exciton reaches the donor-acceptor interface before it recombines, the generated free charges must be extracted over continuous percolation pathways directly to the respective electrodes without being trapped or getting lost by charge recombination.

An interpenetrated donor acceptor structure on the nanoscale, as illustrated in Fig. 1d, would considerably improve the exciton diffusion, charge collection and charge transfer efficiency resulting in higher EQE value and so leading to a higher solar cell efficiency (Sagawa et al., 2010). Figure 1d is showing a conceptual design of an ideal structure of donor
and acceptor phases within the heterojunction solar cell. Different nanostructuring approaches for hybrid heterojunction solar cells have been developed to implement such a device structure. A common method is the use of a porous template and the subsequent filling of the pores by a semiconducting material in order to fabricate vertically aligned nanopillars. One possibility to obtain porous templates is the anodic oxidation of Al to alumina, so-called Anodic Aluminum Oxidation (AAO) (Jessensky et al., 1998; Liu, P. A. et al., 2010). Here, vertical channels with diameters between 20 nm to 120 nm are formed by a first electrochemical oxidation and etching step, followed by a 2nd subsequent etching step for pore widening. The pores can be filled by different methods including simple pore filling, electrochemical deposition and vapor-liquid solid (VLS) growth processes. In principle the lengths, diameters and distances of the formed aligned nanopillars and nanowires can be controlled by the respective dimensions of the template and etching conditions. The height can be controlled by the thickness of the aluminium layer. In Fig. 11 a SEM image of an AAO template fabricated in our laboratory is shown. In a similar way the anodization of titanium films can lead to porous TiO$_2$ films and structures. The fabrication of vertically aligned tubes with pore diameters between 10 nm (Chen et al., 2007) and 100 nm (Macák et al., 2005) are reported. The main technical relevant differences to the AAO template is that TiO$_2$ itself is a semiconductor, while Al$_2$O$_3$ is an insulator, and that the pores in the TiO$_2$ template are closed at the bottom towards the ITO and so the filled in semiconducting material is not in contact with the electrode.

![Fig. 11. Left: Side view SEM image of a porous AAO membrane manufactured by anodic oxidation of aluminium at 40 V in the presence of 0.3 M oxalic acid; right: Side view SEM image of porous TiO$_2$ nanotubes fabricated by anodization of titanium. (Macák et al., 2005). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.](image-url)

One notable example for the integration of a nanostructuring method into solar cell device fabrication is the use of AAO templates for the deposition of CdS by a VLS process leading to aligned nanopillars. Subsequent chemical vapor deposition (CVD) of CdTe resulted into a nanostructured all inorganic solar cell with an impressive PCE of ca. 6% (Fan et al., 2009). A few attempts to use vertically aligned nanopillars to obtain nanostructured hybrid solar cells also exist (Kuo et al., 2008; Ravirajan et al., 2006). These approaches resulted so far in devices with significant lower efficiencies compared to state of the art hybrid solar cells without additional nanostructuring steps. One example for the utilization of an AAO template for a nanostructured hybrid solar cell was published by Kuo et al. (Kuo et al., 2008) and is schematically illustrated in Fig. 12a together with its energy level diagram (Fig. 12b). A direct comparison between a nanostructured bulk-heterojunction hybrid solar cell and a bilayer based hybrid solar cell was performed. First, free standing nanopillars of TiO$_2$ were
formed by spin coating of a TiO$_2$ dispersion onto the AAO template. After sintering at 450°C for 1 h and the subsequent removal of the 300 nm thick AAO template by NaOH, the TiO$_2$ nanopillars were obtained. By covering the TiO$_2$ structure with P3HT via spin coating and subsequent evaporation of Au contacts, hybrid solar cells were manufactured with a PCE of 0.512% in comparison to 0.12% for the bilayer structure of the same donor-acceptor material composition. By this method an inverted solar cell was created, using gold as top electrode. A drawback in this design is that donor and acceptor materials are in direct contact with the ITO substrate, where both, holes and electrons, could be extracted leading to additional recombination events at the ITO electrode which lowers the overall solar cell efficiency.

Fig. 12. (a) Schematic illustration of an inverted TiO$_2$/P3HT hybrid solar cell manufactured by Kuo et al. using an AAO template for formation of parallel aligned TiO$_2$ nanopillars subsequently filled by P3HT; (b) Schematic illustration of the energy level diagram of the fabricated hybrid solar cell. Reprinted with permission from [Kuo et al., 2008]. Copyright [2008], American Institute of Physics.

It was demonstrated that by filling of the AAO template with a conjugated polymer, aligned polymer nanopillars were obtained exhibiting an increased hole mobility due to an improved vertical alignment of the polymeric chains within the AAO template (Coakley et al., 2005). The hole mobility rose by a factor of 20 from 3x10$^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ for a flat polymer layer in diode configuration to 6x10$^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ for the aligned polymer inside the AAO pores. After the AAO template was removed the spacings between the obtained polymer pillars can in principle be filled with an acceptor material like e.g. NCs from a deposited dispersion. This leads to a nanostructured hybrid solar cell with an interdigital device structure as illustrated in Fig. 1d.

Since TiO$_2$ is a semiconductor and could already be used as electron acceptor together with a conjugated donor polymer, the pores of a porous TiO$_2$ film could be directly filled with a donor polymer to obtain a nanostructured bulk-heterojunction hybrid film. Recently Lim et al. demonstrated the successful infiltration of P3HT into TiO$_2$ nanotubes of diameters of 60 nm to 80 nm. However, the diameters of the filled pores were above the desired diameters for an efficient charge extraction, so the reproducible and complete filling of the TiO$_2$ nanotubes is still one of the main challenges to be solved before this nanostructuring method can be implemented into hybrid solar cells.

Another method which was successfully applied for the formation of a nanostructured bulk-heterojunction organic solar cell is nanoimprint lithography (NIL). An AAO template was used as a mask for etching a Si substrate using a two-step inductively coupled plasma (ICP) etching process (Aryal et al., 2008). Thereby a silicon mold as shown in Fig. 13a is formed.
This mold is then used for creating NRs in a film of a conjugated polymer (e.g. regioregular P3HT). The created polymeric rods (Fig. 13c) show an increased crystallinity and preferential alignment of the polymer molecules in the vertical direction (Aryal et al., 2009) as well. The spacing between the polymer rods can then be filled with an acceptor material. After the evaporation of a top electrode the hybrid solar cell would be complete.

Kim et al. used NIL to create a nanostructured solar cell combining the molded polydithiophene derivative TDPDT with PCBM leading to a PCE of 0.8% compared to 0.25% of a bilayer structure (Kim et al., 2007).

7. Outlook

Hybrid solar cells are still lagging behind the PCBM based OPV technology in respect of device performance and maturity for commercialization. They are currently under development and evaluation in basic research and have the potential for further significant improvement. The additional absorption of photons by semiconductor NCs, their potential to utilize multiple excitons generation and their higher electron conductivity compared to organic acceptor materials are some of the reasons behind. Novel device structures, the implementation of nanostructuring methods and the development of lower band gap material able to convert the NIR and IR parts of the solar spectrum into electrical energy will probably lead soon to PCE values of 10% and beyond for OPV technologies (Dennler et al., 2009). It is expected that the hybrid solar cell technologies also benefit from this development since device structure, nanostructuring methods and the development of novel low band gap polymers are overlapping aspects with pure OPV approaches. Progress in the development of organic-inorganic hybrid material design will not only be beneficial for the development of hybrid solar cells but also for various applications such as light emitting diodes, photodetectors etc. and have therefore a broader application potential beyond photovoltaics. In addition the energy levels in inorganic-organic hybrid materials can be tuned more easily compared to pure organic composites based on to the size quantization effects occurring in semiconductor nanostructures which might be beneficial for dedicated applications and allows a broad design flexibility for the variation of material composites. Nevertheless one can clearly deduce from Table 1 that in all 1st and 2nd generation of PV technologies, differences between module PCEs and values of the best research cells are
much smaller than in the case of DSSCs, OPV and hybrid solar cell technologies. Therefore the enhancement of the average module efficiencies of 3rd generation solar cells is one key issue to be addressed in order to extend this technology to wide range applications substituting traditional solar panels. In addition long-term stabilities of 3rd generation solar cells have to be improved tremendously to compete with existing PV technologies otherwise their utilization will be limited to small applications in devices with a limited lifetime such as e.g. disposable sensors and actuators. In case of hybrid solar cells the exploration of additional donor-acceptor materials is necessary, in order to replace toxic compounds by more environmental friendly materials.

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The fourth book of the four-volume edition of 'Solar cells' consists chapters that are general in nature and not related specifically to the so-called photovoltaic generations, novel scientific ideas and technical solutions, which has not properly approved. General issues of the efficiency of solar cell and through hydrogen production in photoelectrochemical solar cell are discussed. Considerable attention is paid to the quantum-size effects in solar cells both in general and on specific examples of super-lattices, quantum dots, etc. New materials, such as cuprous oxide as an active material for solar cells, AlSb for use as an absorber layer in p-i-n junction solar cells, InGaAsN as a promising material for multi-junction tandem solar cells, InP in solar cells with MIS structures are discussed. Several chapters are devoted to the analysis of both status and perspective of organic photovoltaics such as polymer/fullerene solar cells, poly(p-phenylene-vinylene) derivatives, photovoltaic textiles, photovoltaic fibers, etc.

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